Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 03 01 0

FWP: Chemistry of Advanced Inorganic Materials

FWP Number: ERKCC01

Program Scope: The goal of this program is to develop a fundamental understanding of how nanoscale dimensions and interfaces impact the physical, chemical and optoelectronic properties of materials. Materials currently under investigation include metal and metal oxide nanoparticles and thin-film ceramics, including chemical solution based buffer layers for high temperature superconductors. The nucleation and growth of inorganic nanoparticles and self-assembly assisted synthesis of mesoporous nanostructures are major research themes. Studies include classes of materials (e.g. nanomaterials) where the combination of synthesis, neutron scattering and advanced modeling can be uniquely applied to nanomaterial-gas adsorption behaviors in the materials chemistry arena (e.g. hydrogen storage, chemically and photonically active materials, gas separation, superconductivity, tribology, biomimetics, etc.). The main activities of this effort are to exploit and develop new synthetic methods to produce novel classes of inorganic and metal oxide nanoscale materials with properties leading to new fundamental knowledge.

Major Program Achievements: Neutron diffraction and high resolution thermodynamic adsorption investigations used to characterize the layering behavior of n-hexane, n-butane and n-pentane thin films on MgO(100) surfaces. *Ab initio* molecular modeling and high resolution inelastic neutron scattering (INS) studies of the low temperature rotational motion of CH_4 thin films on MgO(100) surfaces were combined to demonstrate that CH_4 adsorbs with the two fold axis perpendicular to the (100) plane. Growth of ZnO/In_2O_3 compound nanostructures with tunable Zn/In ratio (In-doped ZnO nanobelts at high growth temperature and Zn-doped In_2O_3 nanowhiskers at low growth temperature), and measurement of their photoluminescence and scintillation properties. Solution grown La_3TaO_7 films on biaxially textured nickel-3 at. % tungsten (Ni-W) substrates showed much improved texture compared to that of the underlying substrate.

Program Impact: Understanding of dynamics and mechanisms of reactions at interfaces as well as the relationship between properties and nanoscale dimensions, and electronic structure of the materials. The efforts of this program will have significant impact in the areas of nanoscience and technology, electric power transmission, solar energy conversion, chemical sensors, gas storage, lubrication and dehydrogenation catalysts and environmentally relevant materials. In FY2006, 21 referred journal publications and 5 invited talks at international conferences

Interactions:
University collaborators include the Univ. of Delaware (H. Glyde), Univ. of Washington (O. Vilches), Cambridge University and BP Institute (S. Clarke), Univ. of Southern Georgia, (J. LoBue), University of Madrid (D. Martin y Marero), Institute Laue Langevin (C. J. Carlile), ISIS (D. Sivia, S. Parker, M. Adams and A. Ramirez-Cuesta), Cambridge University (Ruth Lyden Bell and Ali Alavi). University of Cincinnati (D.L. Shi), University of Georgia (Z. W. Pan), and the University of Tennessee (Z. Xue, J.R. Thompson, R. Hinde)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Editor-in-chief of Journal of Nanomaterials (M. Hu) Editorial Board, Superconductor Science and Technology; Associate Editor, Journal of the American Ceramic Society; Technical Editor, IEEE Trans. On Applied Superconductivity, DOE's Excellent Mentor Award for training summer interns, Nova 50 Award for Technical Accomplishments in Superconductivity (M. Paranthaman)

Personnel Commitments for FY2006 (to Nearest +/- 10%):
D. Beach (70%), M. Paranthaman (10%), M.Z. Hu (50%), J. Z. Larese (UT joint faculty, 50%), A.J. Rondinone (10%), Z. Pan (40%), Postdoc (100%), Support (30%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 895K **FY05 BA** $ 990K **FY06 BA** $ 1025K

Laboratory Name: Oak Ridge National Lab
B&R Code: KC 02 03 01 0

FWP: Polymer-based Multicomponent Materials

FWP Number: ERKCC02

Program Scope: Combining experimental, theoretical and synthetic approaches, we perform fundamental studies of the structure, dynamics and thermodynamics of macromolecular systems to provide a better understanding of the macroscopic properties of advanced polymeric materials. Major experimental tools include synthesis, including anionic polymerization, X-ray and neutron scattering, NMR and neutron spectroscopy, electron and optical microscopies, and state-of-the-art thermal analysis. Simulation and theoretical approaches include molecular dynamics, Monte Carlo, mean field, lattice, and integral equation theory.

Major Program Achievements: Synthesized the first regular (spherical) crosslinked, surface functional polymer nanoparticles having dimensions <10 nm. Silica nanoparticles (17 nm) were functionalized with polystyrene using ATRP chemistry and blended with polystyrene homopolymers and poly(styrene-b-butadiene) diblock copolymers. Particle mixing with PS is controlled by the ratio of graft (M_g) to matrix (M_m) molecular weight, with complete dispersion when $M_m \leq M_g$. However, the blending rules are entirely different with block copolymers, where reasonable dispersion was only obtained at high molecular weights ($M = 4.6x10^5$ g/mol). Identified important mixing rules in the limit where the nanoparticle size is comparable to the lamellar microdomain dimensions. Raman and Inelastic Neutron Spectra were computed from first principles for polymeric materials and for molecular-based systems at the interface with oxides. The fundamental interactions between polymers and solid surfaces (metals, oxides, graphitic systems, and nanotubes) were investigated through detailed quantum chemical modeling. PRISM theory for the structure of polymer nanocomposites was generalized to treat nonspherical filler particles including rod-like, disk-like and complex molecular shapes. PRISM theory quantitatively established that the origin of an unexpected small angle peak in the collective polymer structure factor of silica-PS mixtures was due to the formation of thin thermodynamically controlled bound polymer layers. Reflectivity results showed that the global dynamics of random copolymers are significantly faster than those for a diblock copolymer melt at the same composition. Our data indicate that the local environment around a copolymer is richer in the minor (fast) component, due to the thermodynamics of the mixture, in agreement with our simulations.

Program impact: Provides insights on the microscopic origins of macroscopic properties of polymer solids, melts, blends, alloys and composites, co-polymers, micellar systems, and small molecule analogs. Results have significant impact on the physics, chemistry and synthesis of polymers, the structure and dynamics of polymers, and the statistical mechanics and simulation of macromolecular systems. ~125 refereed papers in last 3 years.

Interactions: National Laboratories: ANL, LANL, LLNL, NIST, Sandia; National and international user facilities: CNMS, HFIR, IPNS, APS, NCNR, LANSCE, ISIS, Risø, Forschungszentrum (Juelich), Saclay; Universities: collaborations/interactions with over fifty US and foreign universities and over 15 companies.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Five APS Fellows; one National Academy of Engineering member; MRS David Turnbull Lectureship Award; APS High Polymer Physics Prize winner; two APS Dillon Medals; former president Neutron Scattering Society of America; Distinguished Scientist/Professor; Chair 2007 Polymers West Gordon Research Conference: two Chairs of APS Polymer Physics Division; an R&D100 Award; Presidential Green Chemistry Challenge Award; Paul W. Schmidt Memorial Award; Arnold Beckman Award; two ACS Doolittle Awards, and many other awards; numerous regional, national, international advisory committees; twenty journal editorial/advisory boards.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
J. W. Mays (ORNL/U. Tenn Distinguished Scientist., 50%), A. Habenschuss (50%), B. K. Annis (40%), V. Urban (20%), M. D. Dadmun (U. Tenn joint faculty., 50%), B. G. Sumpter (20%), G. D. Wignall (10%), Postdoc (100%), Subcontracts (J. G. Curro, Sandia; K. S. Schweizer, U. Ill; F. S. Bates , Univ. Minn.; 85%), Support (20%).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $1,465K **FY05 BA** $1,785K **FY06 BA** $1485

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC0201010, KC0202030, KC020601

FWP: Theoretical Studies of Metals, Alloys, and Ceramics

FWP Number: ERKCM01

Program Scope: First principles theory is used to predict materials properties, relate them to the electronic structure, provide fundamental insights and guide experimental programs in alloy and ceramic development and nanoscience. Molecular dynamics, based on first principles derived potentials, is used to study the influence of nanoscale defects on macroscopic properties. Global optimization and parallel algorithms are used to extend the applicability of first principles approaches to experimentally relevant nanostructures.

Major Program Achievements (over duration of support): Pioneered development of first principles electronic structure methods and their use in guiding alloy and ceramic development including: the KKR-CPA theory of the electronic structure and phase stability of alloys; the parallel SCPW cluster technique and its use in the study of intergranular films and rare earth dopants in ceramics; the parallel LSMS method and spin dynamics calculations of the magnetic structure of alloys and nanostructures. First principles methods have been used to: develop a differential binding energy model to predict the effects of dopants on ceramic grain growth; determine helium defect properties in BCC transition metal hosts; understand the Ni-valence in nickelates; interpret measured magnetic properties of FeGe nanowires; and understand nanocluster formation in ODS alloys. We have developed an understanding of the interaction between moving dislocations and radiation induced nanometer-sized defects using MD simulation and also developed novel global optimization strategies for nanoparticle structural optimization.

Program impact: Our FLAPW calculations have supported alloy design of Ni-, Fe-, and Ti-based aluminides, and Mo-, Ti-based silicides, and have set the standard for first-principles calculations of ordered intermetallics. Our first-principles SCPW studies support forefront ceramics research here and abroad and have provided a basic understanding of microstructure and mechanical properties of structural ceramics. Many KKR-CPA codes used around the world had their genesis in ORNL codes. A version of the constrained local moment method developed at ORNL is being taken up by research groups in Europe. We have played a leadership role in the overall development of the field of radiation materials science and materials applications in fission reactors, the SNS, and future fusion reactors. We are recognized leaders in applying parallel computing to materials science and the development and use of global optimization techniques for nanostructure optimization.

Interactions: Internal - six divisions and ten experimental and theory groups. External: six national laboratories, eight US and seven foreign Universities, three major corporations and four international research institutes. Past and current CRADAs include: IBM, Honeywell, Motorola, and Nonvolatile Electronics, Inc.

Recognitions, Honors, and Awards (at least partly attributable to support under this FWP or subtask):
Selected: ISI 1000 Most Cited Physicists; 2002 TMS Champion H. Mathewson Medal; G. S. Painter: APS Fellow; G. M. Stocks: APS Fellow, Computerworld Smithsonian Laureate (2000), Gordon Bell Award (3); J. Barhen: NASA Space Act Awards (1995, 2002), R&D 100 Award (1998); V. Protopopescu: R&D 100 Award (1998, 2005); R. E. Stoller: Fellow, ASTM; ANS Fusion Energy Division 2004 Outstanding Achievement Award.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
G. M. Stocks (50%), C.-L. Fu (90%), G.S. Painter (90%), R.E. Stoller (30%), Yu. Osetskiy, (40%), D.M. Nicholson (10%), J. Barhen (30%), V. Protopopescu (20%), J.R. Morris (10%), Other Scientific Staff (20%), Postdocs (210%), Subcontracts (210%), Support (110%).

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $2595K **FY05 BA** $2995K **FY06 BA** $3405K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP: Multiscale Mechanical Properties and Alloy Design

FWP Number: ERKCM06

Program Scope: This program, a redirection of the high temperature alloy design effort, develops fundamental understanding of mechanical behavior across multiple length scales in complex multiphase alloys. Of special interest are new mechanical phenomena that cannot be explained by conventional theories including magnetic effects on strength and ductility, stress-induced superelasticity in the absence of obvious structural transformations, and size effects on mechanical properties particularly at small scales. The observed relationships between mechanical properties and microstructural features (controlled, as needed, by innovative processing techniques and characterized by state-of-the-art microanalytical tools) are used to model deformation and fracture processes. This understanding leads to the formulation of broad scientific principles for the design of advanced metallic materials for use in a variety of next-generation energy production and conversion applications.

Major Program Achievements: By generalizing the Nix-Gao theory to arbitrary shape indenters, showed that the indentation size effect for spheres is manifested through radius rather than indentation depth thus allowing size and material (work hardening) effects to be deconvoluted. Developed a new technique to accurately characterize nanoindenter tip geometry which is critical when measuring small-scale mechanical behavior (10~100 nm range). Demonstrated that incipient plasticity begins in metallic glasses at the theoretical shear strength beyond which strain softening occurs resulting in shear localization and brittle fracture. Derived a new expression to predict glass formability of bulk metallic glasses and other noncrystalline systems. Identified magnetic interaction as a new mechanism underlying unusual solid-solution effects. Discovered that moisture-induced environmental embrittlement is the mechanism responsible for the brittleness of many high-symmetry intermetallics. The ductilizing effect of boron was understood and broad scientific principles governing the deformation and fracture behavior of $L1_2$ and $B2$ alloys were uncovered, including a new thermal-vacancy theory for yield strength anomaly.

Program Impact: This program has provided national and international leadership in the field of high-temperature alloy design. Discoveries from this work stimulated worldwide scientific interest and generated whole new fields of inquiry in the area of mechanical behavior of materials. More than 30 symposia/workshops on intermetallic and related alloys were organized by the PIs. Based largely on this research, C. T. Liu, E. P. George, and J. A. Horton, were identified by ISI as being among the world's most-cited authors in materials science during the past 20 years. Scientific principles developed in this task have been utilized in DOE applied programs, including EERE, Fossil Materials, and NNSA. Tech transfer efforts growing out of this research have resulted in >20 patents and >20 licenses to manufacture products for energy-related applications. Recent emphasis on multiscale mechanical properties has had impact already (e.g., 6 *Phys. Rev. Lett*. papers in the past 3 years).

Interactions: Internal—Theory (ERKCM01), X-ray scattering (ERKCS73) and microscopy (ERKCS30, ERLCM03) efforts. External—Universities (including Pennsylvania, Tennessee, Virginia, Brown, Kyoto, Tohoku, Ruhr, and Beijing Science & Tech.), other national laboratories, and domestic and international materials institutes (IMR and NIMS, Japan; MPI, Germany).

Recognitions, Honors and Awards: E. P. George: 2005 MRS Ribbon Award for Outstanding Paper, 2000 Humboldt Award, 1999 ASM Fellow; C. T. Liu: 2004 elected to the National Academy of Engineering, 2001 *Acta Materialia* Gold Medal, 1994 TMS Fellow; J. A. Horton: 2002 ASM Fellow; Z. P. Lu: 2004 *Phys. Rev. Lett.* paper identified by APS as one of the top physics stories of 2004, 2002 *Acta Mater*. paper identified by ISI as a fast-moving-front paper.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
E.P. George (20%), J.A. Horton (30%), C.T. Liu (UT, 25%), J.R. Morris (80%), Z.P. Lu (70%), Postdocs (200%), Support (50%)

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY 04 BA $1353K **FY 05 BA** $1275K **FY 06 BA $**1295K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP: Microstructural Design of Advanced Ceramics

FWP Number: ERKCM07

Program Scope: Theory and experiment combine to define (1) the relationships between the properties of ceramics and the critical length-scale structural characteristics and (2) how these can be tailored during processing to enhance properties. The fundamental design concepts incorporate different length-scale characteristics into theoretical and analytical models that are used to tailor the behavior (e.g., toughness, mechanical reliability, creep resistance) of ceramics. The results provide a quantitative picture of the mechanisms that enhance the mechanical behavior of monolithic ceramics, composites, multilayer systems and coatings.

Major Program Achievements: This project develops the basis for compositional, as well as microstructural, tailoring of the next generation of ceramics for energy applications. Silicon nitride ceramics serve as a model system where amorphous intergranular films, which are ubiquitous in ceramics, impact mechanical behavior, as well as microstructure evolution. Experimental studies demonstrated the substantial impact that secondary additives (i.e., MgO, Al_2O_3) have on fracture resistance of silicon nitrides employing Lu_2O_3 as a primary additive. This indicates that the interfacial region between the Si_3N_4 grain surface and the intergranular film is a critical factor. Atomic resolution observations revealed that rare earth elements establish ordered layers extending from Si_3N_4 grain surface out into amorphous triple point pockets, which will impact deformation behavior at elevated temperatures. In addition, unique closed-form analytical models were developed to overcome the complexity of stress analyses of multilayer systems to resolve multiple mechanics issues and allow one to examine scaling and materials parameters systematically.

Program Impact: Provided theoretical and experimental insights into the microscopic and atomic scale origins of the mechanical behavior of ceramics that address the greatest impediment to the application of ceramics – that of low fracture toughness. The current studies have provided approaches to toughened ceramics, as well as novel design concepts for tailoring the properties of the next generation ceramics. These concepts have now been extended to include the role of atomic-level, as well as microscopic, characteristics.

Interactions:
Internal–Materials Science and Technology Division: Materials Theory (ERKCM01), Electron Microscopy (ERKCS30), and X-Ray Scattering and Microscopy (ERKCS73) Groups.
External–University of Tokyo, Oxford University, University of Tennessee, University of Karlsruhe, Commissariat à l´Énergie Atomique-Saclay, Korean Institute of Machinery and Materials, National Tsing Hua University, Universidad de Extremadura, Spain, Lawrence Berkeley National Laboratory, Industrial Technology Research Institute, Taiwan.

Recognitions, Honors and Awards:
P.F. Becher: member of World Academy of Ceramics; Fellow, American Ceramic Society, member of National Materials Advisory Board (National Academies); Highly Cited Researcher in Materials Science, ISI Web of Knowledge; American Ceramic Society: Edward Orton Lecturer (2006), Society President, Associate Editor of the *Journal of the American Ceramic Society*.
C-H. Hsueh: Fellow of the World Innovation Foundation and the American Ceramic Society; Highly Cited Researcher in Materials Science, ISI Web of Knowledge; Associate Editor, *Journal of the American Ceramic Society*; member editorial board of *Composite Engineering*.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
P. F. Becher (80%), C-H. Hsueh (90%), M. J. Lance (10%), Support Staff (90%)

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY04 BA $1243K **FY05 BA** $1001K **FY06 BA** $981K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 03 0

FWP: Domain Structure and Dynamics in Epitaxial Oxides

FWP Number: ERKCM29

Program Scope: From its inception, the broad scope of our research in thin-film oxides has been the dielectric physics of cooperative phenomena in oxide heterostructures on silicon, with the particular goal of understanding the fundamental length scales that control phase stability. Specifically we are approaching this goal via studies of field effect phenomena in crystalline oxides and studies of dielectric/optical properties in direct-gap chalcogenides. We are now expanding our program around our discovery of a whole class of strain-stabilized photovoltaic, sulfur-based chalcogenides that have direct gap electronic transitions and tunable band gaps. Heteroepitaxy of these compounds on the plentifully available cubic silicon surface will give us the much-sought-for double p-n junction photovoltaic structure that is required for dramatic improvements in solar cell efficiency. From these new chalcogenides, we can select structures and compositions in a double p-n junction device that will cover the complete solar spectrum with the possibility of achieving 40-60% efficiency in a semiconductor-based solar cell.

Major Program Achievements (over duration of support): Pioneered the field of dielectric physics based on crystalline oxides on semiconductors (COS). Demonstrated ferroelectric polarization reversal in a perfectly commensurate thin-film of $BaTiO_3$ on germanium enabling a two-logic transistor state that offers enormous potential for energy savings in a myriad of electronic sensors and devices. Developed a unifying reformulation of the classic Schottky Barrier Problem as it relates to dielectrics on semiconductors. Published our seminal findings in 1998 (*Phys Rev Lett.*). Since that paper, we have followed with several insightful publications, notably two in *Science*, in which the generalities of the physical and electrical structure for these COS systems and the Schottky Barrier work are presented .

Program Impact: Reformulation of the Schottky Barrier Problem is leading to an entirely new view of interface electrodynamics and interface phase thermodynamics that has broad implications in semiconductor/dielectric physics. These epitaxial oxides offer a unique opportunity to investigate the physics of Schottky barrier formation and charge transfer at the semiconductor-oxide interface, a problem that has accompanied us unyieldingly for over sixty years. This is apparent from focused symposia at U.S. and European scientific society meetings (at least two every year for the last five years) as well as commercial and DoD sector interest in technology applications, and our field-leading citation rate. Publications on this work are highly cited and are providing a substantial framework for both fundamental and applied research as these new materials are being developed.

Interactions: Collaboration with ORNL's (Malcolm Stocks, ERKCM01) and NCSU's (Marco Buongiorno Nardelli) theory task for developing the electronic structure characteristics for several oxide/semiconductor systems. A Penn State Ph.D. candidate (Curtis Billman) has finished his thesis work at ORNL on BaSrO and strain effects on silicon.

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
Rodney McKee: Fellow of the American Physical Society, November 2003; International Advisory Committee, European Materials Research Society, Strasbourg Meeting, June 2003; Adjunct Professor at Penn State. McKee, Fred Walker, and Marco Nardelli presented 22 invited talks in major U.S. and European scientific societies (APS, MRS, TMS, ISIF, EMRS, and EPS) in the last 4 years. Twenty U.S. and foreign patents and licensing arrangements since 1998.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
R .A. McKee (60%), F. J. Walker, UT (80%), Support (20%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $393K **FY05 BA** $377K **FY05 BA** $369K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 05 0

FWP: Design and Synthesis of Nanomaterials

FWP Number: ERKCM38

Program Scope: This research is focused on the understanding of mechanisms that control the synthesis of nanostructure material systems. Specifically, our primary focus is on catalytic synthesis of carbon nanostructures and the synthesis of magnetic alloy nanoparticles encapsulated within these carbon nanostructures. The process of formation and evolution of these carbon-catalyst systems involve dynamical reciprocal influences of both components resulting in the intertwined controlled co-synthesis of two nanostructured materials with complementary functions. We investigate the role of the catalyst material composition, crystallographic orientation, and shape on the atomic structure of the resulting carbon nanofibers; the link between the macroscopic parameters of plasma enhanced chemical vapor deposition reactor environments and the atomic scale processes at the catalyst nanoparticles; and the influence of the curved graphitic structure on the evolution of the shape and structure of the catalyst nanoparticle. A second connected theme of this research is to gain insight on the magnetic properties of catalytic nanoparticles and the formation of ordered alloys during and after co-synthesis and after post-synthesis annealing. The fundamental understanding of this co-synthesis process make possible the precise control of synthesis and assembly of magnetic nanoparticles, carbon nanostructures, and their bi-functional combination.

Major Program Achievements (over duration of support): Controlled co-synthesis of FeCo alloy nanoparticles inside carbon nanofibers has been performed for a range of compositions. $FeNi_3$ alloy nanoparticles were synthesized to study the influence of nanoscale confinement on order-disorder phase transition in alloy nanoparticles. The preliminary electron diffraction studies have shown that disordered phase has been stabilized at room temperature. The relationship of catalyst shape, catalyst orientation, growth conditions with growth rate and graphitic carbon structure has been elucidated. We found strong dependence of growth rate and angle of graphene sheets with respect to nanofiber axis. The configuration of a graphitic overlayer on a clean Ni(111) surface have been investigated using density functional theory. A phenomenological model of the interaction between catalyst and graphitic structure has been developed. It indicates an intrinsic instability in the solution for a curved graphite-particle interface near a nanofiber center and has been experimentally observed under certain growth conditions.

Program Impact: Our work at understanding the nature of catalytically grown nanostructures is leading to a degree of controlled synthesis and directed assembly that is already having an impact in areas such as electrodes for batteries and super capacitors, magnetic storage media, and delivery of materials (e.g. genes, proteins, and therapeutic agents) to living cells, biomimetic structures, and field emission devices. The methods developed under the theory component are of general use for first principles simulations of nanoparticle properties.

Interactions: Florida Atlantic University (K. Sorge, T. Leventouri); Brown University: Division of Engineering (K. S. Kumar); University of Tennessee (P. Rack); Dr Yang Wang, Pittsburgh Supercomputer Center.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): M. L. Simpson, invited participant in National Academies Keck Future Initiative Workshop on "Designing Nanostructures at the Interface between Biomedical and Physical Systems."

Personnel Commitments for FY2006 (to Nearest +/- 10%):
M. L. Simpson (40%), Anatoli Melechko (60%), J.C. Wells (10%), Other Scientific Staff (10%), Postdocs (130%), Subcontracts (10%), Support (20%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $535K **FY05 BA $**483K **FY06 BA** $510K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 03 0

FWP: Atomistic Study of Bulk Metallic Glasses

FWP Number: ERKCM40

Program Scope:
The purpose of this project is to develop novel theoretical and experimental approaches to study the atomic level phenomena in metallic glasses. In particular, we study glass transition, atomic transport, glass formation and mechanical deformation of metallic glasses through such approaches and aim at achieving an understanding of the mechanisms of glass formation and deformation at an atomistic level. While the recent development of bulk metallic glasses has drastically improved the prospect of application of metallic glasses as a structural material, the science of metallic glasses, in particular at the atomistic level, is only in its infancy. Our goal is to establish general principles that could guide the effort for further alloy development and improvement.

Major Program Achievements (over duration of support): We have extended our theory of glass formation and glass transition to elucidate the origin of glass formation in terms of atomic scale topological frustration. We have derived the analytical expressions for the glass transition temperature and the liquid fragility using only the microscopic variables (atomic volume and bulk and shear moduli) and without a fitting parameter. The results agree exceptionally well with the experimental data. The theoretical predictions are now tested by the molecular dynamics (MD) simulation using a many-body potential with varying Poisson's ratio. We have connected our theory to the prevailing theories of the field, such as the energy landscape theory and the mode-coupling theory, and provided an atomistic foundation for these theories, since these theories are phenomenological and lack atomistic underpinning. The structural anisotropy induced by creep deformation was studied by diffraction with a high-energy x-ray synchrotron source and a 2-dimensional detector. The results are being compared with predictions by theory and simulation.

Program impact: Our theory of topological fluctuations in liquids and glasses will impact field of glasses at large, not only metallic glasses but also covalent and molecular glasses. While the theories of crystalline solids have been highly developed, the physics of liquids and glasses lag well behind. Our theory will advance this important but less developed field significantly, potentially impacting a wide range of fields from engineering, physics, chemistry, medicine and biology.

Interactions:
Internal – Center for Computational Sciences, Computer Science and Math Division, Alloy Behavior and Design Group (ERKCM06), X-ray Research and Applications Group (ERKCS73), High Temperature Materials Laboratory, HFIR, SNS.
External – Los Alamos National Laboratory, Ames Laboratory, California Institute of Technology, and the University of Virginia.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP): 10 invited talks. 2006 Senior Researcher Prize, ISMANAM, to T. Egami, National Friendship Award with a Gold Medal from the State Council of China to C. T. Liu, who was also appointed Honorary Distinguished Professor of Sichuan University.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
T. Egami (ORNL/UT Distinguished Scientist, 50%), Y.Y. Braiman (70%), J. R. Morris (10%), Postdocs (230%), Subcontracts (UT, 70%), Support (30%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $ 420K (new) **FY05 BA** $ 955K **FY06 BA** $ 740K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 03 0

FWP: Integrated Multiscale Modeling of Molecular Computing Devices

FWP Number: ERKCM41

Program Scope: Self-assembled molecular electronics (ME) systems composed of many single-molecule devices are conceived as the most promising path to future computers with ultra-dense, ultra-fast, molecular-sized components, and as the likely candidate to continue Moore's law beyond silicon technology. However, there exist formidable barriers to their practical implementation. Experiments in ME are both difficult and very expensive. We are developing a comprehensive theoretical and computational framework, especially for the prediction of electron transport in single molecules in their real environment (i.e., in a single-molecule experiment or at a system level in a working device). Significant theoretical and mathematical issues must be resolved to make such modeling capability a reality. In order to address this goal, this proposal brings together a team of experts to address process, device and circuit modeling of molecular electronics and the underlying mathematics in a comprehensive and integrated fashion across time and length scales.

Major Program Achievements (over duration of support): With the materials funding stream of this multi-disciplinary and multi-institution project, ORNL has been focusing upon theory and code for quantum electron transport in molecular and nanoscale systems. Up to this point, we have developed a parallel code for computing quantum transport and made numerous applications to molecular and nanoscale systems including simulation of various atomic microscopies. Our most recent accomplishments include the following.

We have collaborated with the Vanderbilt groups to apply ab initio methods to improve force-field models of the chemical interaction of molecules with the gold surface used to model the Reed experiment. A cluster model has also been developed for comparison with periodic models since the accurate many-body methods can only work on finite systems.

Control of gating in carbon nanotubes via organic doping and mechanical/vibrational deformation has been examined with the very positive conclusion that such control is possible. This presents a possible path to the construction of computing/memory devices. This work has been published in peer reviewed journals.

Our development of a massively parallel transport code has continued, and we have made progress in demonstrating a solution to the inconsistency of the finite/open Hamiltonians used in the principal layer approach. A rigorous comparison of finite and periodic calculations with identical Gaussian bases and all-electron potentials is now underway.

Program Impact: Our new theoretical and computational tools are enabling more rigorous, complete and realistic modeling of molecular electronic devices and are already beginning to answer both fundamental and experimental questions. These codes will be widely available, including distribution as part of NWChem.

Interactions: Center for Nanoscale Materials (ANL) and Center for Nanophase Materials Sciences (ORNL, ERKCZ01); North Carolina State University; Technical University of Toyohashi; Brown University.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
None

Personnel Commitments for FY2006 (to Nearest +/- 10%):
X. G. Zhang (10%), Postdoc (40%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $194K **FY05 BA** $180K **FY06 BA** $180K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 02 0

FWP: Self Assembly of Stable Nanoclusters in Metallic Matrices

FWP Number: ERKCM42

Program Scope: The goal of this program is to conduct basic research on the understanding of the formation mechanism, thermal stability, and hardening behavior of extremely stable nanoclusters in metallic alloys fabricated by mechanical alloying (MA) and innovative processing. Nanophase materials are known to be metastable in nature; consequently, these materials in bulk forms are usable only at relatively low temperatures because of coarsening processes that occur rapidly at elevated temperatures. The study of the scientific issues of these stable nanoclusters will possibly lead to identifying an interesting material state that is capable of extending the useful temperature range of nanophase materials from ambient to elevated temperatures. Initial work focuses on ferritic alloys, with the intention to extend our studies to include other metallic systems containing stable nanoclusters. This research is composed of two major tasks: (1) theoretical and experimental studies of the formation mechanism and thermal stability of stable nanoclusters in metallic systems and (2) experimental investigation and modeling of hardening mechanisms of stable nanoclusters at ambient and elevated temperatures.

Major Program Achievements (over duration of support): Atomic-scale characterization established that these nanoparticles have extraordinary thermal stability even at temperatures close to 1400ºC. Atom probe tomography of the as-milled powder showed these nanoclusters form during the post-mill heat treatment. The annealing time and temperature are therefore the critical parameters for optimizing the size and number density of the nanoclusters and, consequently, determining the mechanical properties and the stability of the alloy. First-principles calculations carried out to understand the high oxygen concentration in the clusters suggest that stable bonding between oxygen and vacancies is necessary. In fact, the oxygen solubility in bcc-Fe can be as high as the concentration of pre-existing vacancies and reaches a supersaturated state if high vacancy defects can be created through non-equilibrium processes. The first-principles results also predict that vacancies play an indispensable role in enhancing the oxygen/cluster binding energy in the presence of Ti and in inducing the attractive Y-O interaction in Fe. In fact, without vacancies, the Y-O interaction is repulsive in the Fe lattice. The strong oxygen-vacancy binding makes stabilization of coherent nanoclusters in the Fe lattice feasible. The first atomic resolution scanning transmission electron microscopy (STEM) images of these materials have been obtained and show the Fe matrix contains clusters with diameters ranging from 2 to 5 nm and an average spacing of ~12 nm. The initial study of hardening behavior by TEM indicates that these clusters are profound barriers to dislocation movement, even at 1100°C.

Program Impact: The existence of nanoclusters that are thermodynamically stable at elevated temperatures is a truly intriguing issue in the materials community because of both the scientific implications of such a phenomenon and the potential applications. By successfully combining theoretical calculations and experimental studies, this project is providing new understanding regarding nanoclusters that are thermodynamically stable at high temperatures. The scientific principles are expected to have broad applicability in the synthesis of next-generation nanostructured materials with high temperature capability for engineering applications.

Interactions: DMSE efforts at ORNL in theory (ERKCM01), electron microscopy (ERKCS18), atom probe (ERKCM03), and alloy design and mechanical properties (ERKCM06); SNS; Berlin Neutron Scattering Center, Hahn-Meitner-Institute, Berlin; Intense Pulse Neutron Source, ANL; Ohio State University; University of Tennessee; Washington University; National Taiwan Ocean University.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
C.T. Liu: Member of National Academy of Engineering, 2004. M. K. Miller: 2004 MSA Cosslett Award; Co-Chair, Focused Interest Group on Atom Probe, MSA. C. L. Fu: ISI 1000 Most Cited Physicists

Personnel Commitments for FY2006 (to Nearest +/- 10%): C. T. Liu (UT, 20%), M. F. Chisholm (20%), C.L. Fu (10%), A.R. Lupini (10%), M. K. Miller (10%), S.J. Pennycook (10%), J.H. Schneibel (10%), X-L. Wang (10%), Other Scientific Staff (20%), Subcontract (Ohio State University, 30%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $390K (new) **FY05 BA** $374K **FY06 BA** $367K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 01 0

FWP: Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon
FWP Number: ERKCM43

Program Scope: Development of a broad science foundation to identify and understand the atomistic mechanisms of metal-assisted hydrogen storage in nanostructured carbons. The research plan is organized on three interactive levels: (1) First principle computations for simulation of hydrogen interactions with graphite-like structures and prediction of optimal material structures and properties; (2) Based on the theoretical calculations, synthesis of appropriately modified metal-doped pitch precursors and preparation of activated carbon fibers, and (3) In-depth examination of the nanostructures of the carbon substrate and metal catalyst particles, and correlation of these structures with the hydrogen storage characteristics of the fibers.

Major Program Achievements (over duration of support): This program was funded late in FY05.

- Developed computational code for Grand Canonical Monte Carlo (GCMC) simulations of H_2 adsorption on carbon structures. Tested several empirical H_2-C potentials against first-principles calculations to examine their accuracy in describing the energetics of adsorption between graphene sheets. Implemented these potentials in the GCMC code.
- Modified processing conditions of Pd-doped activated carbon fibers (Pd-ACF) based on results from in-situ XRD experiments to reduce sintering of Pd particles.
- Demonstrated that H_2 adsorption (at room temperature and 2 MPa) on Pd-ACF is higher than that of the corresponding Pd-free ACF. Showed evidence of the spillover mechanism from the analysis of temperature effects on adsorption isotherms. Initiated in-situ NMR studies to identify the type of hydrogen species in the hydrogen/ACF and hydrogen/Pd-ACF systems.
- Performed simultaneous bright field (BF) and annular dark-field imaging with pixel-to-pixel correlation using scanning transmission electron microscopy. This technique enabled the determination of the carbon nanostructure by simultaneously recording Z-contrast images of the Pd particles to determine their shape, size distribution, and correlation with the local carbon environment.

Program Impact:
This project addresses long-term fundamental research needs in the area of design, modeling, fabrication, and characterization, at the nanoscale level and with atomic precision, of novel materials for energy-related applications. This research will provide a sound understanding of the fundamental factors that influence hydrogen sorption on carbon materials and how they can be manipulated to attain the on-board storage targets for transportation applications.

Interactions:
Significant collaboration with the Center for Advanced Engineering Fibers and Films, Clemson University.
Members of the IEA Hydrogen Implementing Agreement: Project leader for Project No. N-2 ("Effect of metal doping on the hydrogen storage capacity of activated carbon fibers") and participant in Project No. N-1 ("Metal-carbon IEA collaboration"). Other participants include University of Nottingham (UK), Univ. du Québec à Trois-Rivières (Canada), University of Salford (UK), among others. Angela Lueking, Department of Energy and GeoEnvironmental Engineering, Penn State University; modeling of spillover process. Jerzy Leszcynski, Computational Center for Molecular Structure and Interactions, Jackson State University; modeling of carbon structures. John Craig and Terry Udovic, NIST; neutron scattering studies. Francois Beguin, CNRS, France; evaluating the relation between physical adsorption and electrochemical hydrogen storage.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Nidia Gallego: Member of IEA Hydrogen Implementing Agreement Task 22- Solid and Liquid State Hydrogen Storage Materials. Invited talks at AutoPolymers workshop (October 2005), TMS (March 2006), and ACS (September, 2006)
Nidia Gallego, Cristian Contescu and Fred Baker: Members Organizing Committee Carbon 2007 Conference. Members Board of Reviewers for the journal Carbon.

Personnel Commitments for FY2006 (to Nearest +/- 10%):

N.C. Gallego (30%), C.I. Contescu (30%), F.S. Baker (10%), Other Scientific Staff (20%), Postdocs (220%), Subcontract (130%), Support (20%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 BA $0 **FY05 BA** $450 **FY06 BA** $567

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 03 01 0

FWP: Materials for Catalysts
FWP Number: ERKCS05

Program Scope: Explore the synthesis, near surface properties, and chemical activity of materials for heterogeneous catalysis. Investigate unique compositions, structures, and combinations of materials that can only be achieved by vapor deposition synthesis. Elucidate the interactions between the catalyst and support material including the defect composition and mobility, the space charge segregation, and the atomic structure at the support-catalysts interface. Characterize the catalytic activity with simple, but relevant reactions of small molecules. Materials and samples suitable for examination by high resolution electron microscopy, in coordination with the Electron Microscopy of Materials effort (ERKCS18), are emphasized.

Major Program Achievements (over duration of support): Catalyst particles have been vapor deposited onto a tumbling, high-surface-area powder support. This novel process offers a number of practical and scientific advantages compared to the commonly used solution synthesis techniques and eliminates all sources of contamination associated with chemical precursors. Gold nanoparticles have been formed on silica, tungsten oxide, and carbon, syntheses which are difficult by solution chemistry. The particle size, catalytic activity, and thermal stability of the particles on different support materials have been correlated with potential energy calculations. High-resolution *Z*-contract electron microscopy has identified dispersed single atoms, in addition to the nanometer-sized clusters.

High specific surface area catalysts are also formed by co-deposition of both the support and catalyst phases using oblique-angle sputter deposition. Films have been deposited directly onto electrodes for characterization of electrical and electrochemical properties. Electrical studies are beginning to clarify much of the confusing reports found in the literature, where catalytic activity depends strongly on the pre-reaction conditioning.

Analytical tools are being developed for the characterization of the catalyst activity for gas reactions, including new techniques applicable to thin film samples. Primary goals are increased sensitivity to facilitate characterization of very small area samples and integrated techniques permitting physical characterization under reactive conditions. Using a batch reactor and infrared gas-phase measurements, turn-over-frequencies and reaction kinetics have been probed accurately for very small samples.

Program Impact: Application of expertise in ceramic thin-film synthesis, defect properties, ionic and electronic conduction, and electrochemical systems to the important field of catalysis where inorganic materials serve as both catalysts and active support materials provides a different perspective on scientific inquiry in this area. This work has scientific and technological impacts for catalyzed gas and liquid reactions and electrochemically promoted catalysis.

Interactions: Battelle Columbus (J. Sayer), Vanderbilt University (S. Rashkeev), University of Milan, Dipartimento Chim Inorgan Met Organ & Analit (L. Prati), Argonne National Laboratory (K. Carrado), University of Virginia (R. J. Davis), University of Tennessee, Department of Chemistry (C. Barnes), Tennessee Technological University, Department of Chemical Engineering (C. Wang), Department of Materials Science at MIT, Ceramics (Y. M. Chiang), Department of Physics at University of South Florida (H. Srikanth, R. Hajndl, N. Frey); Dow Chemical Corporation, Midland, MI (S. Babinec, M. Somasi)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
National Federal Laboratory Consortium Award of Excellence in Technology Transfer, 2004

Personnel Commitments for FY2006 (to Nearest +/- 10%):
N. J. Dudney (50%), G. Veith (90%), Support (10%)

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY 04 BA $600K **FY 05 BA $**660K **FY 06 BA** $560K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 03 0

FWP: Theory of Condensed Matter

FWP Number: ERKCS08

Program Scope: Research condensed matter physics theory using a broad range of computational and analytic approaches. The work includes the development and extension of modern theories of condensed matter and computational methods as well as applications. Present work includes highly correlated materials, superconductivity; ferroelectrics, materials design, magnetism and magnetic materials, magnetotransport, neutron scattering, multiscale modeling, magnetic nanostructures, molecular electronics, and various aspects of grain boundaries, surfaces, and interfaces. The long term goals are (1) to support and guide experimental research at ORNL and elsewhere, especially neutron science, nanoscience and novel materials discovery and (2) to develop theoretical and computational approaches for designing novel functional materials and nanostructures.

Major Program Achievements: Prediction of novel magnetoelectric materials using first principles calculations and a novel mechanism for ferroelectricity. Discovery of a new spin glass phase in the double exchange model for colossal magnetoresistive manganites and other materials. Use of polynomial expansion methods and numerical simulations to probe the stability of the ordered phases of manganites. Development of an adaptive time-dependent density matrix renormalization group technique for conductance of correlated nanostructures. Established the role of disorder in modifying photoemission spectra and Fermi surface measurements for Na_xCoO_2. Investigation of quantum size effects in Pb films from first principles including the role of the substrate. Investigation of inhomogeneous charge textures stabilized by electron-phonon interactions within the t-J model. Performance of detailed simulations to investigate the adsorption of molecules on nanofacets and the resulting bonding patterns. Establishment of the electronic structure and the features underlying magnetodielectric response in $Ni_3V_2O_8$, $K_2V_3O_8$ and other oxide magnetodielectrics. Explanation of low energy charge excitations in MgB_2 in terms of the interplay of collective and single particle modes.

Program Impact: Numerous invited talks given at international meetings and at universities; Publications in high profile journals: 52 published papers, including 15 *Physical Review Letters*, over period January 1 to December 1, 2006.

Interactions: *Internal*—Center for Computational Sciences, Computer Science and Mathematics Division, Neutron and X-Ray Scattering (ERKCS01, ERKCS73), Electron Microscopy (ERKCS18), Low-Dimensional Physics, Correlated Electron Materials, and Superconductivity (ERKCS74); Center for Nanophase Materials Science (ERKCZ01), Synthesis and Properties of Novel Materials (ERKCS72): *External*—U.S. Universities: Cincinnati, Clemson, Georgetown, Harvard, Oklahoma State, Stanford, Texas A&M, Vanderbilt, William and Mary, and Universities of California (Davis, Irvine, Los Angeles, Santa Barbara, San Diego), Florida, Minnesota, Tennessee, Texas (Austin and Arlington) and Wisconsin.; Other U.S. Laboratories: Geophysical Laboratory, Naval Research Laboratory: Foreign: research institutions in Argentina, Austria, China, Denmark, France, Germany, India, Italy, Japan, and Sweden.

Recognitions, Honors, and Awards: Member of nominating committee for Division of Computational Physics of the APS (A. Moreo); AAAS Fellow (S. Pantelides); 5 APS fellows; ORNL/UT Distinguished Scientist (E. Dagotto); members of several editorial boards.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
D. J. Singh (80%), E. Dagotto (Joint Faculty, ORNL/UT Distinguished Scientist, 50%), A.G. Eguiluz (Joint Faculty, 40%), R. S. Fishman (30%), A. Moreo (Joint Faculty, 50%), S.T. Pantelides (Distinguished Visiting Scientist, 10%), F.A. Reboredo (80%), Z. Zhang (Joint Faculty, 70%); Postdocs (150%), Subcontracts (90%), Support (10%).

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY 04 $1126K **FY 05** $1575K **FY 06** $1780K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 02 0

FWP: Electron Microscopy of Materials

FWP Number: ERKCS18

Program Scope: New techniques are developed for the investigation of materials with sub-Ångstrom resolution and single atom-sensitivity using aberration-corrected scanning transmission electron microscopes. These techniques focus on *Z*-contrast imaging and electron energy loss spectroscopy to allow elemental identification of single atoms within their bulk environment and determination of their local electronic structure. Data from microscopy is combined with first-principles theory to provide insights into key issues in condensed matter physics, chemical sciences and nanoscience. Increasing emphasis is being placed on quantitative comparison to theoretical image simulations for both *Z*-contrast microscopy and electron energy loss spectroscopy.

Major Program Achievements: Achieved the first direct imaging of a material with sub-Ångstrom resolution and the first spectroscopic identification of a single atom within a bulk material. A new definition of image resolution was proposed based on a criterion of 10% contrast. Imaging and lattice location of surface atoms on a rough, insulating oxide surface was achieved. Direct imaging of the "charge-ordered" stripes in a mixed-valence manganite. First imaging of light oxygen columns in crystals by Z-contrast imaging and simultaneous phase contrast imaging. Atomic resolution spectroscopic mapping of carriers across the chains and planes of a superconductor. Imaging of charge-ordered nanoclusters representing spontaneous electronic phase separation.

Program Impact: Results have stimulated the commercial development of aberration-corrected scanning transmission electron microscopes, which are now offered by all manufacturers as standard, and are finding increasing demand worldwide, with over 30 currently on order. Major centers now all include a state-of-the-art aberration-corrected scanning transmission electron microscope, or plan to add one in the near future. We have demonstrated over the last 10 years how coupling microscopy with first-principles theory offers quantitative insights into the atomic origins of materials properties, and this has become general practice. Papers have been accepted in high impact journals *Science*, *Nature*, *Nature Materials*, and *Physical Review Letters*, *Proceedings of the National Academy of Science*, as well as in longer more specialized journals. Numerous review articles have appeared in encyclopedias and books. Program is actively involved in educational outreach with visits from university professors, teachers and students at all levels.

Interactions: *Internal*—Materials Science and Technology Division: Theory Group (ERKCS08), Thin Film and Nanostructures efforts (ERKCS05, ERKCS72), Correlated Electron Materials Group (ERKCS74); Chemical Sciences Division: Surface Chemistry and Heterogeneous Catalysis Group (ERKCC47).
External—Universities: Vanderbilt; North Carolina State; North Carolina A&T; Drexel; Northwestern; Dartmouth College; Tokyo, Japan; Melbourne, Australia; Madrid, Spain; Pohang, Korea, Seoul National, Korea. National Institutes: LBNL, ANL, BNL, FS-MRL (TEAM); Polish Institute of Physics, Warsaw, Poland; Chinese Academy of Sciences, Beijing, China; Industries: Nion, Pixon, Fischione.

Recognitions, Honors, and Awards: Institute of Physics Thomas J. Young Medal and Award, 2001, Fellow of the American Association for the Advancement of Science, 2004. Group members presented 19 invited talks in FY 2006.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
S.J. Pennycook (10%), M.F. Chisholm (40%), A.R. Lupini (50%), M. Varela (20%), Postdocs (120%), Support (100%)

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY 04 $755K **FY 05** $955K **FY 06** $1055K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 01 01 0

FWP: Atomistic Mechanisms in Interface Science—Direct Imaging and Theoretical Modeling

FWP Number: ERKCS30

Program Scope: Aberration-corrected scanning transmission electron microscopes with sub-Ångstrom beams are used to image the atomic structure of interfaces and grain boundaries with single atom-sensitivity. Electron energy loss spectroscopy allows elemental identification of single atoms at interfaces and determination of local electronic structure. Data from microscopy is combined with first-principles theory to provide insights into key issues in interface science in metals and alloys, structural ceramics, quasicrystals, complex oxides, superconductors and semiconductor device structures.

Major Program Achievements: The instrumental advances of the aberration correction program, leading to the first direct imaging of a material with sub-Ångstrom resolution, and the first spectroscopic identification of a single atom within a bulk material, have allowed significant breakthroughs in interface science. In structural ceramics, the first imaging of dopant atoms in the glassy phase at a grain boundary was made, with first-principles modeling of mechanical behavior. A new dislocation core structure was identified in a complex intermetallic, explaining its brittle behavior at low temperatures. The role of Ca doping in enhancing the critical current capacity of a superconductor grain boundary was determined by a combination of imaging, spectroscopy and first-principles theory. Application of the 3D confocal imaging technique to a high dielectric constant device has shown the 3D location of individual hafnium atoms within the active region, a key unsolved challenge on the semiconductor industry roadmap.

Program Impact: Results have stimulated the widespread application of aberration-corrected scanning transmission electron microscopes, and major centers now all include such instruments or plan to add one in the near future. We have demonstrated over the last 10 years how coupling microscopy with first-principles theory offers quantitative insights into the atomic origins of materials properties, and this has become general practice. Papers have been accepted in high impact journals *Science*, *Nature*, *Nature Materials*, *Physical Review Letters*, and the *Proceedings of the National Academy of Science*, as well as in more specialized journals. Numerous review articles have appeared in encyclopedias and books. Program is actively involved in educational outreach with visits from university professors, teachers and students at all levels.

Interactions: *Internal*—Materials Science and Technology Division: Materials Theory (ERKCM01), Thin Film and Nanostructures (ERKCS72), Correlated Electron Materials (ERKCS74), Ceramic Science (ERKCM07), and Alloying Behavior and Design (ERKCM06) Groups; Chemical Sciences Division: Surface Chemistry and Heterogeneous Catalysis Group (ERKCC47).
External—Universities: Vanderbilt; North Carolina State; North Carolina A&T; Drexel; Northwestern; Washington; Tokyo, Japan; Melbourne, Australia; Madrid, Spain; Pohang, Korea, Seoul National, Korea. National Institutes: Polish Institute of Physics, Warsaw, Poland; Chinese Academy of Sciences, Beijing, China; Industries: Nion, Pixon, Fischione, Sematech, Alcoa.

Recognitions, Honors, and Awards: Institute of Physics Thomas J. Young Medal and Award, 2001, Fellow of the American Association for the Advancement of Science, 2004. Group members presented 19 invited talks in FY 2006.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
S. J. Pennycook (10%), M. F. Chisholm (40%), G. Duscher (Visiting Scientist, 50%), D. Kumar (Visiting Scientist, 40%), S. T. Pantelides (Distinguished Visiting Scientist, 20%), M. Varela (70%), Postdocs (250%), Subcontracts (90%), Support (100%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY 04 $1045K **FY 05** $1033K **FY 06** $1123K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 02 0

FWP: Functional Nanomaterials: Growth Mechanisms and Properties

FWP Number: ERKCS72

Program Scope: This program addresses the two central challenges of nanoscale science: First, to understand complex, self-organizing behavior and, second, to control growth mechanisms and direct the assembly of materials with enhanced or entirely new combinations of properties. The materials focus is on epitaxial heterostructures of complex metal oxides grown with atomic-layer control, and on carbon and other nano-tubes/fibers/wires/belts that exhibit effects of reduced and experimentally variable dimensionality, including ordered arrays. The program's strength is its integration of three key capabilities: advanced synthesis, detailed characterization (nanoscale to bulk), and modeling/simulation. For synthesis, emphasis is placed on energetic-beam methods—pulsed-laser deposition (PLD), laser vaporization, and plasma-enhanced CVD—and on time-resolved, in situ diagnostics of growth and kinetics. For ex situ characterization, scanning probes, electron microscopy, and electronic, magnetic, and transport measurements are used. Theory and experiment are integrated for understanding both growth and properties. Microsecond time-resolved surface synchrotron x-ray diffraction (SSXRD) at the Advanced Photon Source is used with modeling to study surface evolution during PLD, in order to kinetically manipulate oxide growth. Effects of nanoscale structure, confinement, chemical attachment, and interlayer coupling on functional properties are studied.

Major Program Achievements: Observed antiferroelectricity in $BiCrO_3$ multiferroic films. Experimentally verified a strain-insensitivity of the ferroelectric polarization in $BiFeO_3$ and $Pb(Zr,Ti)O_3$ films. Used surface x-ray scattering to quantitatively determine the evolution of a $SrTiO_3$ surface during pulsed laser deposition, and demonstrated that the so-called "layer-by-layer" growth involves more than two layers at any time. Discovery of high-k dielectric perovskites with practical crystallization temperatures. Developed imaging and interferometry techniques to directly measure growth kinetics of carbon nanotube arrays, enabling the formation for a quantitative model. Developed the scientific understanding of factors governing catalyst efficiency in nanotube growth.

Program Impact: Work is at the forefront of developing the science basis for the design and synthesis of artificial oxide heterostructures with enhanced properties and for understanding nonequilibrium growth environments such as pulsed laser vaporization processes for thin film and single-wall carbon nanotube growth. Definitive exploration of TMO cooperative phenomena, and development and testing of theoretical models. Development of nano-structured materials for efficient energy use: multi-layered oxide-film fuel cells, aligned carbon nanotube thermal interface materials, multifunctional nanotube-based polymer composites, and efficient solid-state lighting.

Interactions: *External*—Collaboration/subcontract on macroscopic aligned SWNT arrays with Rice University). Other collaborations with universities (41). Other collaborations on carbon-based materials with Argonne, Brookhaven, and Sandia. Collaborations with 21 other U.S. and foreign national/industrial research labs. *Internal*—Numerous interactions at ORNL involving fundamental chemistry, effects of strength and thermal transport in polymer nanocomposites, electronic enhancements in organic electronics and sensors, and environmental effects. Oxide heterostructures synthesized with atomic-layer control are indispensable to test theory/modeling using leadership scientific computing facilities, and to exploit atomic-scale spectroscopy based on *Z*-contrast scanning transmission electron microscopy.

Recognitions, Honors, and Awards (at least partially attributable to support under this FWP): Many invited talks at national/international conferences/workshops; several ORNL research recognition awards; several invention disclosures/patents.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
H. M. Christen (30%), D. B. Geohegan (30%), G. Eres (50%), G. E. Jellison, Jr. (10%), B. C. Larson (10%), H. N. Lee (90%), D. H. Lowndes (10%), M. Pan (20%), A. A. Puretzky (40%), C. M. Rouleau (50%), J .Z. Tischler (20%), Postdocs (120%), Subcontracts (460%), Support (60%).

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY 04 $2350K **FY 05** $2175K **FY 06** $2175K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 01 0

FWP: X-Ray Scattering and Microscopy

FWP Number: ERKCS73

Program Scope: This program performs fundamental investigations of materials microstructure and evolution on mesoscopic length scales and atomic scale investigations of local chemical ordering and the dynamical electronic structure of materials. High-brilliance synchrotron x-ray beams at the Advanced Photon Source (APS) are exploited in connection with innovative instrumentation, advanced measurement techniques, and theory collaborations. Advanced x-ray focusing optics and three-dimensional (3D) submicron-resolution x-ray microscopy techniques are developed to probe materials microstructure and evolution on mesoscopic length scales. Novel neutron optics and new scattering techniques are developed to extend neutron diffraction investigations to 3D measurements of materials structure and sample sizes on length scales of tens of microns. Long-standing materials issues associated with 3D grain-growth, deformation, and strain localization are addressed using microbeams. Non-resonant inelastic x-ray scattering is used to study the dynamical electronic structure of strongly correlated electron materials, elastic diffuse scattering is used to probe short-range atomic structure in alloys, and Bragg scattering is used to study strain and phase in bulk materials and the structure and epitaxy of thin-films.

Major Program Achievements: Developed 3D x-ray structural microscopy for submicron-resolution investigations of crystal microstructure and strain tensor distributions; demonstrated sub-100 nm polychromatic x-ray focusing optics, and polychromatic neutron optics with less than 100 μm; developed polychromatic microdiffraction beam line on UNICAT-II (Sector 34) at the APS; performed the first micron-resolution, nondestructive, 3D measurements of thermal grain-growth and intra-granular dislocation density tensors; absolute, measurement of plastic deformation with submicron resolution over mesoscopic length scales using microindents; combined inelastic x-ray scattering with energy-resolved Wannier function analyses to identify new symmetry selection rules in strongly correlated materials; pioneered new methods to study fundamental properties of solid solution alloys.

Program Impact: The development of 3D x-ray structural microscopy provides direct, quantitative links between mesoscale microstructural measurements and first-principles-based theory and modeling that are needed to develop a predictive understanding of materials behavior; the development of the only x-ray facility providing 3D crystal structure, orientation, and local elastic and plastic strain tensors with submicron resolution; The development of x-ray optics and polychromatic microbeam analyses that are being integrated into synchrotron microbeam facilities worldwide; demonstrated the sensitivity of non-resonant inelastic x-ray scattering measurements combined with Wannier function analyses sensitivity to symmetry breaking in strongly correlated materials; Showed that polychromatic neutron focusing optics can increase neutron fluxes by two orders of magnitude for sub-100 micron beams, which will facilitate neutron scattering measurements in small sample volumes.

Interactions: External–NIST; APS, ALS, ESRF, Canadian, Australian, and Pohang (Korea) Synchrotron facilities; LANSCE, IPNS, and Chalk River; MPI-Düsseldorf; Otto-von-Guericke-Universität, Magdeburg, Germany; BNL; 14 universities; Alcoa Technical Center; Northrup-Grumman; Ford Motor Company; General Motors; IBM; Industrial Whiskers Fundamental Task Force; NASA. Internal–oxide film growth (ERKCS72), correlated electron materials (ERKCS74), mechanical behavior (ERKCM06).

Recognitions, Honors, and Awards: 2005 Maslen Fellow (GI), R&D 100 Award (2000) (JB); 2 American Physical Society Fellows (BL,GI), ASM Fellow (GI), Co-editor *Journal of Synchrotron Radiation* (GI); Guest Editor, *MRS Bulletin* (March 2004, BL); UT-Battelle Scientific Research by Team Award (2002, GI,BL); CHESS Policy and Advisory Board (BL); Chair, APS Beam Time Allocation Committee (2002–2006, JT); Chair, APS User's Organization Steering Committee (2006-2007, GI), NSLS-II Experimental Facilities Committee (2006, GI); more than 30 invited talks (2004–2006).

Personnel Commitments for FY2006 (to Nearest +/- 10%):
B.C. Larson (90%), G. E. Ice (80%), J.D. Budai (100%), J. Pang (100%), C.M. Rouleau (10%); E.D. Specht (50%), J.Z. Tischler (80%), Guest Scientists: R. Barabash (100%), Y. Puzyrev (80%), Support (50%).

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY 04 $2150K **FY 05** $2450K **FY 06** $2375K

Laboratory Name: Oak Ridge National Laboratory
B&R Code: KC 02 02 02 0

FWP: Materials by Design
FWP Number: ERKCS74

Program Scope: The focus of this program is science-driven synthesis and fabrication of new materials with novel properties and functionality. This is accomplished by a two-pronged approach involving (1) the development and growth of crystalline materials with innovative properties and (2) a "materials-by-design" approach using molecular beam epitaxy (MBE), laser MBE, and other novel growth processes to control properties with environment and dimensionality. One main theme of the research is to control and design materials that display complex, cooperative phenomena such as superconductivity, magnetism, metal-insulator transitions, ferroelectricity, optoelectricity, and optomagnetism. An essential component of this program is the development of advanced instrumentation and measurement techniques to characterize the functionality of these materials.

Major Program Achievements: Discovery of Luttinger-liquid physics in quasi-one-dimensional $Li_{0.9}Mo_6O_{17}$ by scanning tunneling microscopy and photoemission, *Phys. Rev. Lett.* **95**, 186402 (2005) and *Phys. Rev. Lett.* **96**, 196403 (2006). Observation of dopant-induced nanoscale electronic imhomogeneities in $Ca_{2-x}Sr_xRuO_4$, *Phys. Rev. Lett.* **96**, 66401 (2006). First grown and studied the physical properties of Ba_2CoO_4 single crystals, *Phys. Rev. B* **73**, 174404 (2006). Direct evidence of Eu atom tunneling at 450 MHz in crystalline $Eu_8Ga_{16}Ge_{30}$, *Phys. Rev. Lett.* **97**, 017401 (2006). Self-assembled, strong flux-pinning columnar defects formed by $BaZrO_3$ in YBCO result in high performance high T_C superconducting wires, *Science* **311**, 1911 (2006). Discovered new class of model compounds for studying the anomalous Hall effect, *Phys. Rev. B* **73**, 224435 (2006). Observation of Kondo lattice behavior in ordered dilute magnetic semiconductor $Yb_{14-x}La_xMnSb_{11}$, *Phys. Rev. B* **72**, 205207 (2005). Characterized inversion breaking structural phase transition in $Cd_2Re_2O_7$ using second harmonic generation, *Nature Physics* **2**, 605 (2006). FeGe nanowires on Ge that are strong ferromagnets below 200 K, *Phys. Rev. Lett.* **96**, 127201 (2006). Realized robust superconductivity in ultrathin, quantum-confined films of Pb, with strongly contrasting interactions of vortices with differing quantum structural defects, *Nature Physics* **2**, 173 (2006). Observation of giant discrete steps in metal-insulator transition in perovskite manganite wires, *Phys. Rev. Lett.* **97**, 167201 (2006). Showed that vortices are pinned predominantly by large, sparse nonsuperconductive inclusions in a class of $YBa_2Cu_3O_{7-\delta}$ thin films, *Phys. Rev. B* **73**, 134502 (2006). Developed switching spectroscopy piezoresponse force microscopy, *Rev. Sci. Instr.* **77**, 073702 (2006). Simultaneous formation of nanodots and surface ripples through phase decomposition processes, *Appl. Phys. Lett.* **88**, 093112 (2006). Discovered new complex dielectric phenomena in doped perovskite materials, *Phys. Rev. B* **74**, 054101 (2006).

Program Impact: Program has produced >40 papers and >45 invited talks at national and international meetings in recent years.

Interactions: Extensive collaborations exist within ORNL. There are ~70 national and international collaborations leading to published papers and joint external proposals.

Recognitions, Honors, and Awards (at least partly attributable to support under this FWP): E. W. Plummer, National Academy of Science; Guangbiao Lecture Professor at Zhejiang University, Hangzhau University, China. J. Shen, Guangbiao Chair Professor at Zhejiang University, Hangzhau, China; Outstanding Young Researcher Award by Chinese National Science Foundation. S. Kalinin**,** ORNL Early Career Accomplishment Award for Science and Technology. A. Baddorf, S. Kalinin, S. Jesse, and B. Rodriguez, Team Scientific Research Award from ORNL; ORNL Director Award for Team Achievement.

Personnel Commitments for FY2006 (to Nearest +/- 10%):
A. P. Baddorf (10%); L. A. Boatner (20%); D. K. Christen (20%); Z. Gai (10%); G.E. Jellison, Jr. (10%), R. Jin (100%); S. V. Kalinin (20%); D. G. Mandrus (80%); M. Pan (10%); E. W. Plummer (ORNL/UT Distinguished Scientist, 25%); B.C. Sales (90%); J. Shen (10%) J. R. Thompson (10%); H. H. Weitering (joint UT faculty, 30%); J. F. Wendelken (20%); Postdocs (410%), Subcontracts (390%), Support (100%).

Authorized Budget (BA) for FY 04, FY 05, FY 06:
FY 04 $2858K **FY 05** $3005K **FY 06** $3145K